RANDOM COPOLYMER BLENDS OF STYRENE, PARA-FLUORO STYRENE AND ORTHO-FLUORO STYRENE

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Random copolymer blends of styrene, *para*-fluoro styrene and *ortho*-fluoro styrene

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This study completes the investigation of the phase behaviour of polymer blends involving styrene (S), *ortho*-fluoro styrene (oFS) and *para*-fluoro styrene (pFS). As before, due to the proximity of the glass transition temperatures of most blends investigated, the miscibility or immiscibility is established using the alternative thermal analysis method based on enthalpy recovery of samples annealed in the glassy state. In most respects the phase behaviour is similar to that of the corresponding chlorinated systems. The value of the Flory–Huggins parameter $\chi_{S,oFS}$ is much smaller than $\chi_{S,pFS}$. However, the latter is approximately the same as $\chi_{oFS,pFS}$ and, as a consequence, a miscibility window as found in the system PS/P(oClS-*co*-pClS) is only present in PS/P(oFS-*co*-pFS) blends for rather low molecular weights.

(Keywords: copolymer blends; phase behaviour; intramolecular repulsion; styrene; fluorinated styrene)

Introduction

In the last decade many studies on polymer–polymer miscibility have focused on systems involving random copolymers. In contrast to polymer blends involving homopolymers only, it is believed that specific interactions are not a necessary requirement for miscibility in such systems. In the usual theoretical discussion of systems involving random copolymers, the free energy is expressed in terms of the Flory–Huggins theory with an effective χ-parameter depending on the different binary χ-parameters involved in the mean field[1–3]. These χ-parameters contain all the contributions to the free energy of mixing except for the ideal entropy of mixing and hence, not surprisingly, are complicated functions of composition and temperature.

One of the principal goals of these studies on random copolymer blends is to reach a stage where it is possible to predict polymer–polymer miscibility on the basis of a database of χ-parameter values. The determination of these values, for instance χ_{AB}, is most simply accomplished by studying the critical copolymer composition x for which polymer P(A) and random copolymer P(A_x-*co*-B_{1-x}) are on the borderline of miscibility. However, in view of the above discussion, this value could, in principle, differ from that obtained from a similar study on the miscibility of P(B) and P(A_x-*co*-B_{1-x}). In fact, this is exactly what has been observed for blends consisting of styrene (S) and methyl methacrylate (MMA), i.e. A = S and B = MMA[4]. These differences can be related to the sequence distribution of the copolymer. Possible modifications of the simple theoretical model to account for this have been discussed[5]. A striking experimental example was published very recently: blends of a random copolymer P($S_{0.5}$-*co*-$MMA_{0.5}$) and PMMA exhibited only partial miscibility, whereas blends of the corresponding alternating copolymer P(S-*alt*-MMA) were completely miscible with the same PMMA[6]. A different but related observation concerns the influence of the tacticity of the components on their miscibility; again PMMA is a striking example, i.e. the miscibility of PMMA with poly(vinyl chloride) is strongly dependent on the tacticity of PMMA[7]. These examples clearly demonstrate the difficulties in establishing the aforementioned database. Despite these limitations, the predictive scheme based on available χ-parameter values has been quite successful so far, mainly because the values are apparently not too sensitive to the approximations and assumptions involved in their evaluation. The precise location of so-called windows of miscibility may differ somewhat from the predicted location, but the effect is usually only a slight shift of the borderline of the miscibility window. This has been demonstrated convincingly by a large body of experimental results on a variety of systems. Many examples can be found in a recent review paper by Cowie[8].

In the past we have demonstrated the ability to predict miscibility regions in other blends, by predicting the phase behaviour in blends of polystyrene (PS) and random copolymers of *ortho*-chloro styrene and *para*-chloro styrene, P(oClS-*co*-pClS), on the basis of χ-parameter values obtained by the analysis of the phase behaviour of blends of random copolymers of chlorinated styrenes and poly(oxy-2,6-dimethyl-1,4-phenylene) (PPE)[2,9]. A similar study has now been completed for blends of PS and random copolymers of fluorinated styrenes. Part of the motivation for studying these systems came from the observation that, due to the proximity of the glass transition temperatures of all components involved, these systems are ideally suited for an investigation by the recently introduced enthalpy relaxation procedure[10]. In a previous paper we studied

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blends of S and random copolymers of S and *ortho*-fluoro sytrene (oFS) and reported a value for $\chi_{S,oFS}$ of approximately 0.01 based on S as the unit[11]. Here we report the results on blends of PS and random copolymers of S and *para*-fluoro styrene (pFS). From this a value of 0.06 for $\chi_{S,pFS}$ is found. Together with the same value of 0.06 for $\chi_{oFS,pFS}$, established before from the phase behaviour in blends of PPE and random copolymers of S and fluorinated styrenes, the phase behaviour in various other blends involving S and fluorinated styrenes is predicted and verified. Again, the 'intramolecular repulsion' model or binary 'interaction' model is shown to give a consistent and reliable description of the phase behaviour.

Experiment

Materials. PS with a weight average molecular weight, M_w, of 40000 (PS_{40}) was synthesized anionically. PS with M_w of 7000 (PS_7) was obtained from Aldrich Chemical Co. and PS (Styron 666) from Dow Chemicals. All copolymers were prepared by free radical polymerization in toluene. The polymerization was stopped at 60% conversion to prevent copolymer composition drift. The molecular weights were determined by gel permeation chromatography at 25°C using chloroform as an eluent. The copolymer compositions were determined by i.r. and ^{13}C n.m.r. Values of M_w and M_n were calculated relative to PS standards. Glass transition temperatures and molecular weights are shown in *Table 1*.

Blends were obtained by coprecipitation from 5 wt% toluene solution into a 20× excess of methanol. The blends were dried under vacuum at a temperature just below the glass transition temperature. The composition of most blends was 50/50 wt%, but compositions rich in PS_7 were also investigated.

Calorimetric measurements. Differential scanning calorimetry (d.s.c.) experiments were performed using a Perkin-Elmer DSC-7. A heating rate of 20 K min^{-1} was employed. Samples for enthalpy relaxation experiments were prepared by pressing the dry powder of the polymer blends into tablets and sealing in small d.s.c. pans. Before annealing, the samples were kept at an appropriate temperature in the melt. The samples were then quenched in liquid nitrogen followed by annealing for different times, t_a, at a temperature, $T_a = 90°C$. Subsequently, a scan was taken from 0 to 200°C, followed by rapid cooling and a second scan.

Table 1 Sample characterization

Sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	T_g (°C)
PS_7	7	6	87
PS_{25}	25	15	98.5
PS_{40}	40	32	101
PS(Styron)	326	113	105
$P(S\text{-}oFS_{18})$[a]	103	55	101
$P(S\text{-}oFS_{40})$	117	59	97
$P(S\text{-}oFS_{49})$	106	53	95
$P(S\text{-}oFS_{77})$	131	71	93
$P(S\text{-}pFS_{8})$	84	47	102
$P(S\text{-}pFS_{16})$	84	47	102
$P(S\text{-}pFS_{25})$	84	49	104
$P(S\text{-}pFS_{46})$	114	64	104
$P(S\text{-}pFS_{67})$	84	48	103
$P(oFS\text{-}pFS_{10})$	133	68	92
$P(oFS\text{-}pFS_{23})$	124	60	95

[a]Numbers indicate mole fraction of given monomer in the copolymers

Results

In the usual mean-field description of random copolymer blends involving a homopolymer P(C) and a random copolymer $P(A_x\text{-}co\text{-}B_{1-x})$ the free energy of mixing is given by a Flory–Huggins type expression with an effective χ-parameter given by[2]:

$$\chi = x\chi_{AC} + (1-x)\chi_{BC} - x(1-x)\chi_{AB} \qquad (1)$$

The last term represents the reduction in the number of A–B contacts upon mixing. If these contacts are relatively unfavourable, for certain values of x χ may become sufficiently small, or even negative, to produce miscibility. This particular situation is often referred to as the 'intramolecular repulsion effect' for obvious reasons.

Equation (1) can be used to predict the miscibility in these blends provided the values of the χ-parameters involved are known. The simplest way to determine, for instance, χ_{AB} is by investigating the miscibility of blends of P(A) or P(B) and $P(A_x\text{-}co\text{-}B_{1-x})$. In the first case, the effective χ-parameter is given by:

$$\chi = (1-x)^2\chi_{AB} \qquad (2)$$

This expression arises because the amount of A–B contacts increases upon mixing. Once the critical value of x, i.e. the value for which the system is on the borderline of miscibility, is determined, the value of χ_{AB} follows by equating χ to:

$$\chi_c = 1/2[(N_{w1})^{-1/2} + (N_{w2})^{-1/2}]^2 \qquad (3)$$

where N_{w1} and N_{w2} are the weight average chain lengths based on a fixed unit, S in our case.

One of the objectives in the area of random copolymer blends is to find random copolymers with a strong intramolecular repulsion, which could consequently be miscible with many different homopolymers. This is of interest for making homogeneous blends, but also in the area of composites. In the latter case, polymeric compatibilizers, usually block copolymers, play a very important role, based on the selective miscibility of the blocks of the copolymer with homopolymers involved. A whole new area is developing now around the so-called iniferter technique by which block copolymers, with blocks consisting of chemically uniform random copolymers, can be synthesized[12].

As equation (2) shows, the determination of large χ-parameter values involves random copolymers that differ only slightly from the corresponding homopolymer, i.e. x close to 1 for the situation described in the last paragraph. In that case the difference in glass transition temperatures will be rather small and the well known composition-dependent single glass transition temperature criterion for miscibility no longer works. In previous publications we demonstrated the usefulness of an alternative thermal analysis procedure based on enthalpy recovery of samples annealed in the glassy state for these types of situation[10,11,13]. In this paper, polymer blends involving S, oFS and pFS are considered. Large values of the χ-parameters involved are not expected, but all polymers have nearly the same glass transition temperature and therefore, besides being of interest from the point of view of phase behaviour in random copolymer blends and the concept of intramolecular

repulsion, the systems are ideally suited for an enthalpy recovery study.

Figures 1 and *2* show characteristic thermograms of blends of PS/P(S–pFS$_{16}$) and PS/P(S–pFS$_{25}$) obtained by annealing at 90°C samples quenched from the melt state. Clearly, the first system is homogeneous and the second is phase separated. This situation is found for all temperatures of the melt state between 120 and 240°C. Based on these measurements, a value of 0.06 was determined for $\chi_{S,pFS}$. The values of $\chi_{S,oFS}$ and $\chi_{oFS,pFS}$ were determined previously[11,14], the latter from the phase behaviour observed in blends of PPE. *Table 2* contains these χ-parameter values together with those of the corresponding chlorinated systems taken from ref. 9.

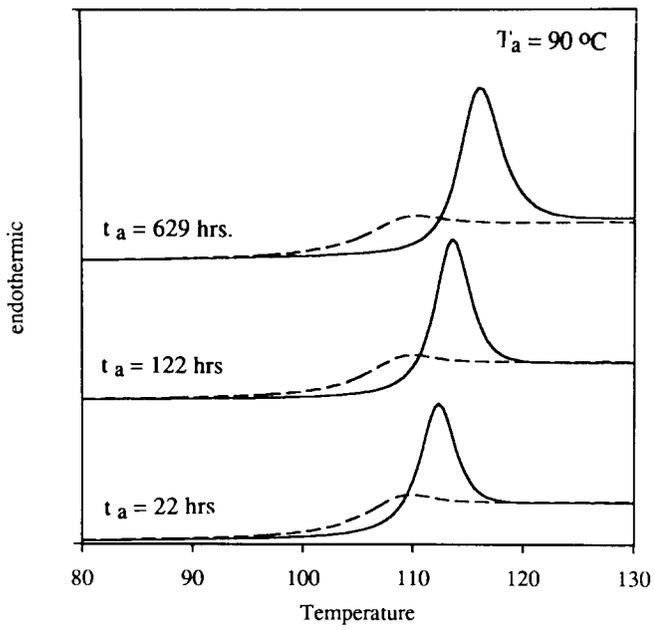

Figure 1 Characteristic thermograms of PS$_{40}$/P(S-*co*-pFS$_{16}$) blends annealed for 5 min at 200°C and subsequently aged at 90°C for the times indicated. ——, First scan; - - - - -, second scan

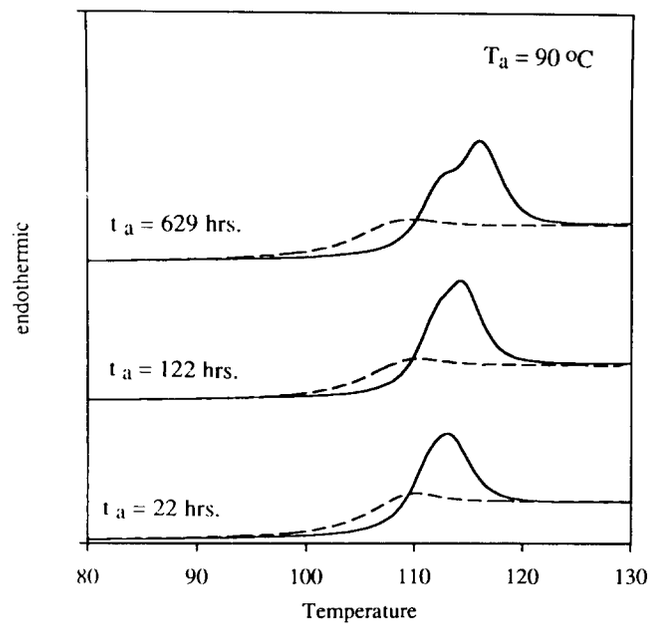

Figure 2 Characteristic thermograms of PS$_{40}$/P(S-*co*-pFS$_{25}$) blends annealed for 5 min at 200°C and subsequently aged at 90°C for the times indicated. ——, First scan; - - - - -, second scan

Table 2 Segmental χ-parameters at 200°C

Segment pair	χ_{ij}	Segment pair	χ_{ij}
$\chi_{S,oFS}$	0.01	$\chi_{S,oClS}$	0.005
$\chi_{S,pFS}$	0.06	$\chi_{S,pClS}$	0.07
$\chi_{oFS,pFS}$	0.06	$\chi_{oClS,pClS}$	0.10

Table 3 Phase behaviour

Blend	Miscible	Phase separated
PS$_{25}$/P(S–oFS$_x$)	x = 18, 40, 49	x = 77
PS(Styron)/P(S–oFS$_x$)	x = 18	x = 40, 49, 77
PS$_{40}$/P(S–pFS$_x$)	x = 8, 16	x = 25, 46, 67
PS(Styron)/P(S–PFS$_x$)	x = 8, 16	x = 25, 46, 67
P(S–oFS$_{49}$)/P(S–oFS$_{77}$)	Miscible	
P(S–oFS$_{18}$)/P(S–oFS$_{40}$)	Miscible	
P(S–oFS$_{18}$)/P(S–oFS$_{77}$)	Phase separated	
PS$_7$/P(oFS–pFS$_{10}$)	*LCST* ≃ 140°C	
PS$_7$/P(oFS–pFS$_{23}$)	*LCST* ≃ 140°C	
P(oFS–pFS$_{10}$)/P(oFS–pFS$_{23}$)	Miscible	

A comparison between the chlorinated and the fluorinated system shows that in both cases the *ortho* substitution has only a minor effect; the χ-parameter values with respect to S are rather small. The effect of the *para* substitution is much larger. Furthermore, the χ-parameter between oClS and pClS is larger than between either oClS or pClS and S. This implies that in blends of PS and P(oClS$_x$-*co*-pClS$_{1-x}$) a miscibility window, i.e. miscibility for a range of x values, could be present due to the intramolecular repulsion within the random copolymer. This miscibility window is indeed observed in a manner predicted by the simple theoretical model briefly discussed before. However, it should be noted that the minimum of the χ-parameter value for these blends as a function of the random copolymer composition is slightly positive, 0.002 at x = 0.825. Therefore miscibility does require the molecular weights of the polymers involved not to exceed about 100 000 and the miscibility window, centred around x = 0.825, will be wider for smaller molecular weights.

For the corresponding fluorinated system PS/P(oFS$_x$-*co*-pFS$_{1-x}$) equation (1) predicts a minimum for the blend χ-parameter of 0.0096 at x = 0.92. This value of the χ-parameter is substantially larger than for the chlorinated systems and consequently miscibility requires much lower molecular weights. Given the fact that the random copolymers used here had a molecular weight slightly exceeding 100 000, on the basis of equation (3) miscibility is expected to occur for molecular weights of PS somewhat below 10 000 for values of x ranging from 1 to approximately 0.7. As shown in *Table 3*, which summarizes the miscibility studies performed, this is exactly what happens. For PS$_7$ a lower critical solution temperature (*LCST*) is found in blends with the appropriate random copolymers of oFS and pFS at 140°C. It is important to realize that the value of $\chi_{oFS,pFS}$ was determined previously from miscibility studies involving PPE; in other words this agreement between predicted and observed phase behaviour is another demonstration of the reliability of the simple random copolymer theory. All the observed phase behaviours

summarized in *Table 3* are consistent with the values reported in *Table 2*.

Conclusions

The phase behaviour of blends involving styrene and fluorinated styrenes resembles, in many respects, that of the chlorinated systems. In both cases, the effect of *ortho* substitution is considerably smaller than that of the *para* substitution. There is a subtle but essential difference between blends of polystryene and random copolymers of *ortho*- and *para*-chloro styrene and the corresponding blends of polystyrene and random copolymers of *ortho*- and *para*-fluoro sytrene. In the former blend, the intramolecular repulsion in the copolymer component is strong enough to give rise to a miscibility window for common molecular weights. In the fluorinated systems, however, the intramolecular repulsion, in the sense that the interaction parameter between the monomers of the random copolymer is larger than the two other parameters involved, is absent and miscibility only occurs at much lower molecular weights. The molecular reason for this difference is as yet unclear.

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